

# The Heats of Formation of $\text{C}_3\text{H}_7^+$ and $\text{C}_2\text{H}_5^+$ Determined by Pulsed Field Ionization-Photoelectron Photoion Coincidence Spectroscopy

T. Baer<sup>1</sup> W.-W. Chen<sup>2</sup> J.-B. Liu<sup>2</sup> Y. Song<sup>2,3</sup> X.-M Qian<sup>2,3</sup> and C. Y. Ng<sup>3</sup>

<sup>1</sup>Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA

<sup>2</sup>Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory,  
University of California, Berkeley, California 94720, USA

<sup>3</sup>Ames Laboratory, U. S. DOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

## INTRODUCTION

The dissociation dynamics and dissociation onsets for ionic reactions have been investigated by the successful technique of threshold photoelectron photoion coincidence (TPEPICO) spectrometry. However, it has proven difficult to improve the resolution of TPE spectroscopy to better than about 5 meV. Recently, we have developed a high resolution PEPICO method based on pulsed field ionization (PFI) of high- $n$  Rydberg states. This experiment has the capability of selecting the ions with sub-millivolt resolution and thus to provide us with a very precise measure of the dissociative ionization onsets for the ionic reactions. It is almost an order of magnitude improvement in the resolution of the ion energy compared to the previous TPEPICO experiment.

The dissociation of  $\text{C}_2\text{H}_5\text{Br}^+$  and  $2\text{-C}_3\text{H}_7\text{X}^+$  ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) was investigated by this new PFI-PEPICO method, and the accurate values for the heats of formation of  $\text{C}_2\text{H}_5^+$  and  $\text{C}_3\text{H}_7^+$  were determined. The ionic fragmentation often occurs in the Franck-Condon gap between the ion's electronic states, it is of interest to find that PFI-PEs are also produced in these Franck-Condon gaps which makes the PFI-PEPICO method possible.

## EXPERIMENT

Synchrotron radiation from a U10 undulator is dispersed by a 6.5m monochromator. The ring, operated in the multi-bunch mode, generates 512 ns of quasi-continuous radiation followed by a 144 ns dark gap. The photons excite the molecular beam cooled sample in the presence of a 0.2 V/cm electric field to energies in the vicinity of the dissociative ionization threshold. While the promptly produced electrons and ions are extracted by this small dc field, neutrals in high- $n$  Rydberg states remain in the ion source. These high- $n$  Rydberg states are then field ionized during the 144 ns dark gap by a 7 V/cm, 200 ns long pulsed electric field. The PFI electrons are collected in a 5 ns window which serves to discriminate against all non-field-ionized electrons that are produced by direct ionization. The ions are extracted by the constant DC field of 0.2 V/cm as well as by the 1.52 MHz, 7 V/cm pulsed field. The average electric field in this quasi-continuous acceleration region is about 3 V/cm. The ions are accelerated to a final energy of 120 eV through three acceleration regions, and travel with this energy through the 40cm long drift tube where they are detected by a set of microchannel plates. The PFI electrons provide the start signal for a Stanford Research Systems multi-channel scaler with a maximum resolution of 5 ns. The ion TOF resolution used in this study is 40 ns per channel. Time-of-flight spectra are collected at fixed photon energies, and all ions are collected with no suppression of "false" ions.

All the samples have vapor pressures that are below atmospheric pressure and so the samples were seeded in a molecular beam of Ar. Argon was passed at a pressure of about 1 atmosphere over a liquid sample. The translational temperature of the molecular beam as measured from the TOF Peak widths was about 30 K, however, this is not necessarily a good measure of the internal energy of the molecules in the beam.

## RESULTS

### (a) $C_3H_7^+$

Figure 1 shows the typical PFI-PEPICO TOF spectra of  $2-C_3H_7Cl^+$  and  $C_3H_7^+$  ions at several photon energies near the dissociation onset. In the experiments, the typical signal levels were about 1-10 c/s PFI electrons, 2,000-20,000 c/s ions, and 0.1-1 c/s coincidence for a total counting time of about 1-2 hours. The net parent and daughter ion areas were obtained by subtracting the false coincidence background from the total signal. They were divided by the total net parent and daughter ion areas and plotted as a function of the photon energy. This breakdown diagram is shown in Figure 2. It shows that at low energies, only the parent ion is stable, but that as the dissociation onset is approached, the fraction of parent ions slowly diminishes, until it reaches zero at 11.085 eV.

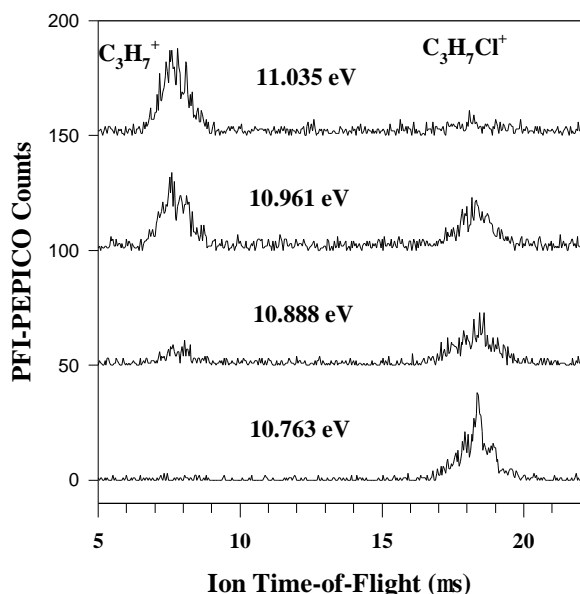


Figure 1. The typical PFI-PEPICO Time-of-Flight distributions of  $C_3H_7^+$  and  $2-C_3H_7Cl^+$  in the vicinity of the dissociation limit.

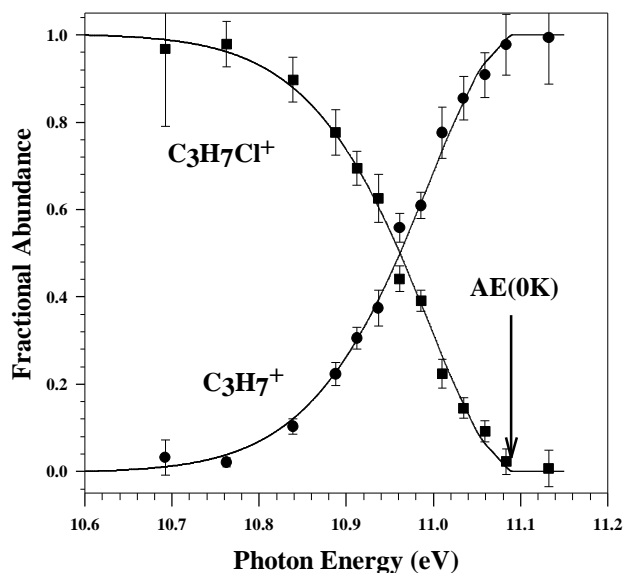


Figure 2. The breakdown diagram for  $2-C_3H_7Cl^+$  in the vicinity of the Cl loss dissociation limit. The 0K dissociation limit is indicated by the arrow.

The breakdown diagram for  $2-C_3H_7Cl^+$  could be fitted by assuming that the broadening of the breakdown diagram is due solely to the thermal energy in the  $2-C_3H_7Cl$  molecule. Its thermal energy distribution could be described as:

$$P(E, T) = r(E) e^{-E/RT} / \int_0^\infty r(E) e^{-E/RT} dE \quad (1)$$

where  $\rho(E)$  is the density of the ro-vibrational states.

The solid lines in Fig. 2 were obtained by convoluting this thermal energy distribution with a step function at the dissociation limit (AE) as given by Equations (2) and (3):

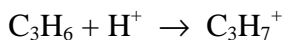
$$Daughter(h\nu) = \int_{AE-h\nu \text{ or } 0}^{\infty} P(E, T) dE \quad (2)$$

$$Parent(h\nu) = \int_0^{AE-h\nu \text{ or } 0} P(E, T) dE \quad (3)$$

The important point is that the information of interest, which is the 0 K dissociation limit (AE), is independent of how the breakdown diagram is fitted. This 0 K limit is the point in the breakdown diagram at which the parent ion signal disappears. The only effect of the thermal sample is to change the slope at which this onset is approached. The derived 0 K onset for  $\text{C}_3\text{H}_7^+$  ions from 2- $\text{C}_3\text{H}_7\text{Cl}$  is  $11.085 \pm 0.005$  eV, indicated by an arrow in Fig. 2.

The similar breakdown diagrams for 2- $\text{C}_3\text{H}_7\text{Br}$  and 2- $\text{C}_3\text{H}_7\text{I}$  are also obtained. Their derived 0K onsets for  $\text{C}_3\text{H}_7^+$  ions are  $10.455 \pm 0.010$  eV,  $9.851 \pm 0.02$  eV from 2- $\text{C}_3\text{H}_7\text{Br}$  and 2- $\text{C}_3\text{H}_7\text{I}$ , respectively. With the auxiliary heats of formation for the precursor 2- $\text{C}_3\text{H}_7\text{X}$  molecules, and the X atoms, the measured onsets could be converted into the heats of formation of  $\text{C}_3\text{H}_7^+$ . The derived heats formation of  $\text{C}_3\text{H}_7^+$  at 0K are  $825.4 \pm 0.8$ ,  $822.3 \pm 2.0$  and  $824.0 \pm 2.0$  kJ/mol from 2- $\text{C}_3\text{H}_7\text{Cl}$ , 2- $\text{C}_3\text{H}_7\text{Br}$  and 2- $\text{C}_3\text{H}_7\text{I}$ , respectively. Although they are on the high side compared to previous measurements, they agree very well with each other. Because of the quality of the breakdown diagram and the best precision of the neutral 2- $\text{C}_3\text{H}_7\text{Cl}$  heat of formation, we tend to favor the results from this molecule. If we weight our three measurements according to their precision, we propose an average value of a  $\text{H}^0_{\text{f}, 0\text{K}}$   $824.3 \pm 1.2$  kJ/mol or a  $\text{H}^0_{\text{f}, 298\text{K}}$  of  $805.9 \pm 1.2$  kJ/mol. It is 7.5 kJ/mol higher than the previously accepted value.

The heat of formation of  $\text{C}_3\text{H}_7^+$  could be converted to a proton affinity (PA) of  $\text{C}_3\text{H}_6$  using equation:



which yields:

$$\text{PA}(\text{C}_3\text{H}_6) = -\text{H}^0_{\text{f}}(\text{C}_3\text{H}_7^+) + \text{H}^0_{\text{f}}(\text{H}^+) + \text{H}^0_{\text{f}}(\text{C}_3\text{H}_6)$$

at both 0K and 298 K. Using the known heats of formation of  $\text{H}^+$  and  $\text{C}_3\text{H}_6$  at 0K and 298K, we derive the proton affinities of  $\text{C}_3\text{H}_6$ , which are  $739.0 \pm 1.2$  kJ/mol and  $744.1 \pm 1.2$  kJ/mol at 0K and 298 K, respectively. The new values are in near perfect agreement with several high level ab initio calculations.

#### (b) $\text{C}_2\text{H}_5^+$

The PFI-PEPICO time-of-flight spectra of  $\text{C}_2\text{H}_5\text{Br}^+$  and  $\text{C}_2\text{H}_5^+$  ions at the photon energies near its dissociation onset have also been measured, and its breakdown diagram are obtained, from which the 0K appearance energy of  $\text{C}_2\text{H}_5^+$  is determined as  $11.130 \pm 0.005$  eV with the help of simulation. The ionization energy of  $\text{C}_2\text{H}_5\text{Br}$  was measured as  $10.307 \pm 0.002$  eV from its PFI spectrum. The derived  $\text{C}_2\text{H}_5^+$  heats of formation are  $900.5 \pm 2.0$  kJ/mol at 298 K, and  $913.2 \pm 2.0$  kJ/mol at 0K. We also obtain an ethylene proton affinity which ranges from 681.9 to 678.5 kJ/mol, this can be compared to the “accepted” value of 680.5 kJ/mol, and a calculated value of 681.9 kJ/mol.

## REFERENCES

1. C. W. Hsu, M. Evans, C. Y. Ng and P. Heimann, *Rev. Sci. Instrum.* 1997, **68**, 1694.
2. G. K. Jarvis, Y. Song and C.Y. Ng, *Rev. Sci. Instrum.* 1999, **70**, 2615.
3. G. K. Jarvis, K. M. Weitzel, M. Malow, T. Baer, Y. Song and C. Y. Ng, *Rev. Sci. Instrum.* 1999, **70**, 3892.
4. T. Baer, Y. Song, C.Y. Ng, J.-B. Liu and W.-W. Chen, *J. Phys. Chem. A* 1999, **in press**.

This work was supported by the Chemical Sciences Division of the U. S. Department of Energy under contracts DE-AC03-76SF00098 and DE-FG02-97ER14776.

Principal investigator: Prof. C. Y. Ng, Ames Laboratory, U. S. DOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA. Email: cyng@ames.gov. Telephone: 515-294-4225.